Rearrangement: Migration to electron deficient Nitrogen

Hofmann Rearrangement: The reaction of amide with bromine in alkaline medium gives an amine with one carbon less than that of starting amide is known as Hofmann Rearrangement. It is also known as Hofmann degradation reaction.

$$R-CO-NH_2 + Br_2 + NaOH = R-NH_2 + CO_2 + NaBr$$

Mechanism:

Evidences:

- 1. The intermediates bromoamide, salt of bromoamide and alkyl isocyanate have been isolated.
- 2. The rearrangement is intramolecular in nature. No cross-over products are obtained in cross over experiments.
- 3. Further prove of intramolecularity is obtained when the reaction is done with optically active α -phenyl propanamide we get optically active α -phenyl ethylamine with retention in configuration.

Curtius rearrangement: This rearrangement is closely related to Hofmann rearrangement. In this reaction an acyl azide is heated in benzene to form alkyl isocyanate which on hydrolysis gives the corresponding amine.

Mechanism:

The acyl azide can be synthesised in the following ways

Lossen rearrangement: This rearrangement is also very similar to Hofmann and Curtius rearrangements. This reaction consists of conversion of hydroxamic acid to alkyl isocyanate on treatment with strong inorganic acid or to conversion of o-acetyl hydroxamic acid to alkyl isocyanate on treatment with base.

Mechanism:

In base medium: